THE INFLUENCE OF SOLUBLE SALTS IN THE SLIP ON THE PROPERTIES OF ENAMELS

BY

THOMAS LEONARD HURST

B.S., University of North Carolina (Raleigh Unit), 1936
M.S., University of Washington, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN ENGINEERING IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1940

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THE INFLUENCE OF SOLUBLE SALTS PRESENT IN THE SLIP ON THE PROPERTIES OF ENAMELS

I. INTRODUCTION

A. General Statement

Soluble salts in enamel slips have long been associated with difficulties involved in handling the slips and with defects which developed in the fired enamels. Only mediocre success has been reported in identifying the true causes of these defects and in tracing the role played by these salts in the development of the finished enamel.

The soluble salts in enamels can be traced to three main sources, (1) to the water used for milling, (2) to the mill additions, and (3) to the solution of the frit. The first two sources can be controlled so as to obtain the best results at all times, while the third source, because of the nature of the frit and the variable character of the grinding process constitutes an unknown quantity which further increases the importance of understanding the influence of soluble salts present in the slips.

B. Review of the Literature

Pertinent literature on the effects of soluble salts in enamels is rather limited. Several writers have reported the effects of the ratio $Na_2O : B_2O_3$ on the consistency and working properties of enamel slips. From the standpoint of slip behavior, McIntyre[1] reported that a ratio of $Na_2O : B_2O_3$ equal to 0.89 served as a boundary between good and poor slips. Those slips having a lower ratio were easy to work, while higher ratios increased the difficulties in handling. The ratio 0.89 itself produced slips which were generally good.

Cook[2] and others[3,4,10] reported that the presence of borax in the slip accompanied surface defects such as tearing and crawling. Cooke[3] identified crystals of sodium borate, sodium carbonate, sodium fluoride, and sodium sulphate in the dried enamels and reported that borax aggravated tearing. References to the various effects of certain salts on the set of enamel slips and on the metal base are frequent, and in good agreement with each other. Rosenberg[5] found that surface hardening and brushing difficulties were aggravated by high quantities of borax and boric acid in the slip.

He attributed tearing to the shrinkage of borax during melting, and the surface tension of the molten material.

Theories have recently been advanced to explain the widespread and rather successful use of special electrolytes such as sodium nitrite, to correct tearing and improve film strength. Both Lange[6] and Rosenberg reported that tearing was reduced by sodium nitrite because this salt melted at low temperature, wetted the enamel, and bonded it together until the film was completely fused. Rosenberg claimed the function was purely mechanical. Hartshorn[7] proposed a closer control of the $Na_2O : B_2O_3$ ratio in enamel slips by removing part of the mill liquor and replacing it with solutions of known concentrations of salt. He found that additions of sodium nitrite corrected tearing in enamels in which the original sodium oxide : boric oxide ratios varied widely. Howe[8] believed that slow drying by conduction rather than by convection reduced tearing.

C. Object and Scope of the Study

Since previous studies of the effects of salts on enamel films were concerned mostly with phenomena associated with tearing and crawling, and not with the actual fundamental causes of film strength, this investigation had as its objective the determination of the factors responsible for tearing of enamels and the mechanism by which good film strength was developed.

In this study, enamel film strength was defined as that property of an enamel coating which permits it to resist disruption during the operations of drying and firing.

With the foregoing objective in mind, the problem was investigated from these points of view: (1) the effects of solution of the frit, (2) the effects of selective crystallization of the materials dissolved from the frit, (3) the effects of the use of electrolytes on the film strength of enamels, and (4) a physical-chemical study of the systems of salts that are present in enamels and their influences on tearing and film strength. These systems were considered to be independent of the frit glass, and of great influence and importance on the strength of the films at temperatures below the fusion of the enamel.

II. PROCEDURES

Six typical sheet steel cover coat frits were selected for study. Of these, two were ordinary opaque, three were super opaque, and one was acid resistant. These frits were milled with distilled water only, under definite conditions of time and temperature to various finenesses. Fineness tests were made in duplicate and were checked

to within 0.5 gr. residue on a No. 200 sieve from a 50 cc. sample of slip. The mill liquors were filtered from the slips, and portions of each were evaporated. The residues which represented the products of the solution of the frit were analyzed petrographically, spectroscopically, and by X-rays. Determinations of the specific gravities, the weight residues per gram of liquor, and the pH values were also made on all the liquors.

The exchangeable ions introduced into the slips during milling were identified by passing the mill liquors through prepared clay and permutite, removing the exchanged ions by standard methods and analyzing the extract spectroscopically. The effects of several salts on the behavior of enamel slips were investigated by base exchange and pH studies. The usual procedures for these determinations were followed and observations were made chiefly on the reactions produced by the additions of solutions of sodium fluoride, sodium chloride, sodium metaborate and sodium phosphate to clay suspensions.

Ground frits were dried, and the particle sizes, shapes and size distributions were determined for the portions which were collected between sieves No. 200 and 325. Microscopic observations and projection methods described by Berger[11], Tooley[12], and others were employed for this study.

The effects of single electrolytes on the properties of enamels were investigated by dry grinding the frit, then adding clay, distilled water, and electrolyte premixed in the proper proportions. Enamels sprayed at 40 grams per square foot and fired from 600° to 1500° F. in intervals of 100° were examined for surface properties and film strength.

The relationship between sodium oxide and boric oxide in the fused enamel was studied by preparing enamels in the same manner, the only variable being the electrolyte additions. The total amount of electrolyte was maintained at 1 lb. total sodium oxide plus boric oxide per 100 lb. frit (or 3.35 oz. oxide per gal. water), while the $Na_2O : B_2O_3$ ratio was varied through a range from 0.0656 to 2.220. Boric oxide was always added as boric acid, while sodium oxide was introduced first by sodium nitrite and sodium hydroxide, and later by many other sodium salts. These enamels were sprayed at 40 grams per square foot, dried, and fired from 1000° to 1500° F. in 100° intervals. Observations were made of the drying behavior, especially the selective crystallization of the electrolytes, the firing behavior and the film strength of the fired enamels.

Guided by the results of the foregoing studies, various other salts were added to enamels which were prepared in the same manner. The salts were selected on the basis of (1) eutectic composition, (2) high melting combinations, (3) the presence of ions other than sodium, and (4) their degree of solubility. These electrolytes were added in equi-molecular ratios with boric acid in amounts sufficient to provide 1 lb. total oxide equivalent per 100 lb. frit. The enamels were sprayed, dried, and fired, and the drying behaviors, brushing qualities and tearing resistances were observed.

III. RESULTS AND DISCUSSION

A. Analytical Results

Analyses of mill liquors showed that increased fineness of grinding increased the total solution of the frit and that the pH values of the liquors approached a condition of equilibrium on continued grinding. Solution of the frit was a leaching process rather than a true solution. The total quantity of salts in solution was more important than the ionized portion. Therefore the pH values serve as no criteria for slip properties and film strength.

The residues of dried mill liquors consist of sodium fluoride, borax, sodium metaborate, sodium metasilicate, sodium carbonate, sodium sulphate, and a gel of silica with a trace of alumina.

The shapes, sizes and size distributions of the frit particles are very similar regardless of frit composition, and cannot be correlated with the film strength of enamels.

In the absence of mill added electrolytes, sodium, potassium and calcium are the most abundant cations in enamel slips. The use of sodium phosphate to facilitate grinding is made possible by the adsorption of the phosphate ion by the clay. This increases the base exchange capacity of the clay and increases the deflocculation of the system. The effects of soluble fluorides and nitrites on slips can only be explained by similar anion exchanges.

Each electrolyte has a definite and characteristic effect on the enamel films. For example, films containing boric acid are extremely hard and brittle, while those with magnesium carbonate are soft and fluffy. Shorelining and surface scumming result when sodium sulphate is present, while additions of sodium nitrite with sodium sulphate reduce shorelining and improve the surface gloss.

The carbon residues produced by firing enamels which contain metal-organic salts, and the colors developed by additions of colored inorganic salts show that most salts precipitate principally on the

surface of the films, and that shorelining is associated with the rhythmic precipitation of these salts during drying.

Tearing and poor film strength always result when boric acid is added to enamels, while proper additions of sodium nitrite, sodium hydroxide, and some other salts with boric acid eliminate this trouble.

The resistance to tearing is definitely associated with the ratio of $Na_2O : B_2O_3$ in the slip. This fact is illustrated in figure 1. The best tearing resistance is obtained at a ratio of 0.89, which is that of sodium metaborate. Ratios from 0.89 to approximately 0.55 offer good but decreasing resistance to tearing. The actual ratio in this range at which tearing appears, depends on the total quantity of salts in the slip. Ratios less than 0.55 permit tearing even with very small amounts of salt present, while as the total salt content increases the more nearly must the ratio 0.89 be approached by corrective additions of sodium salts (or rarely but possibly, H_3BO_3), to prevent tearing and give maximum film strength.

Salts other than sodium nitrite and sodium hydroxide were used with fair success. Tearing was eliminated, but other defects such as blistering, pitting, and scumming were usually encountered, and were caused chiefly by the failure to eliminate the anions of the salts before fusion of the enamel.

B. Causes of Tearing

Experimental work indicated that boric acid causes tearing. Boric acid crystallizes in concentrated interlaced crystals on the surface of the film and in random network systems on the ground coat at the cover coat-ground coat interface. These depositions are closely associated with the low solubility of boric acid and the important effects of the first crystal in seeding the system.[14] During drying, the water drawn toward the surface of the film carries with it the dissolved salt, and much of the boric acid crystallizes in concentrated, interlaced sheaves on the surface. This takes place early in drying because of the low solubility of boric acid in water. A large proportion of the capillary openings are sealed, broken or obstructed by the salt deposition and the drying of the clay, and consequently further diffusion of water to the surface is impeded. Cracks, extending in random fashion across the surface, developed in the enamel due to drying shrinkage and case hardening. Capillary attraction draws the water entrapped beneath the surface to the cracks where it evaporates and deposits the salts which it contains. Therefore boric acid crystals are deposited on the surface of

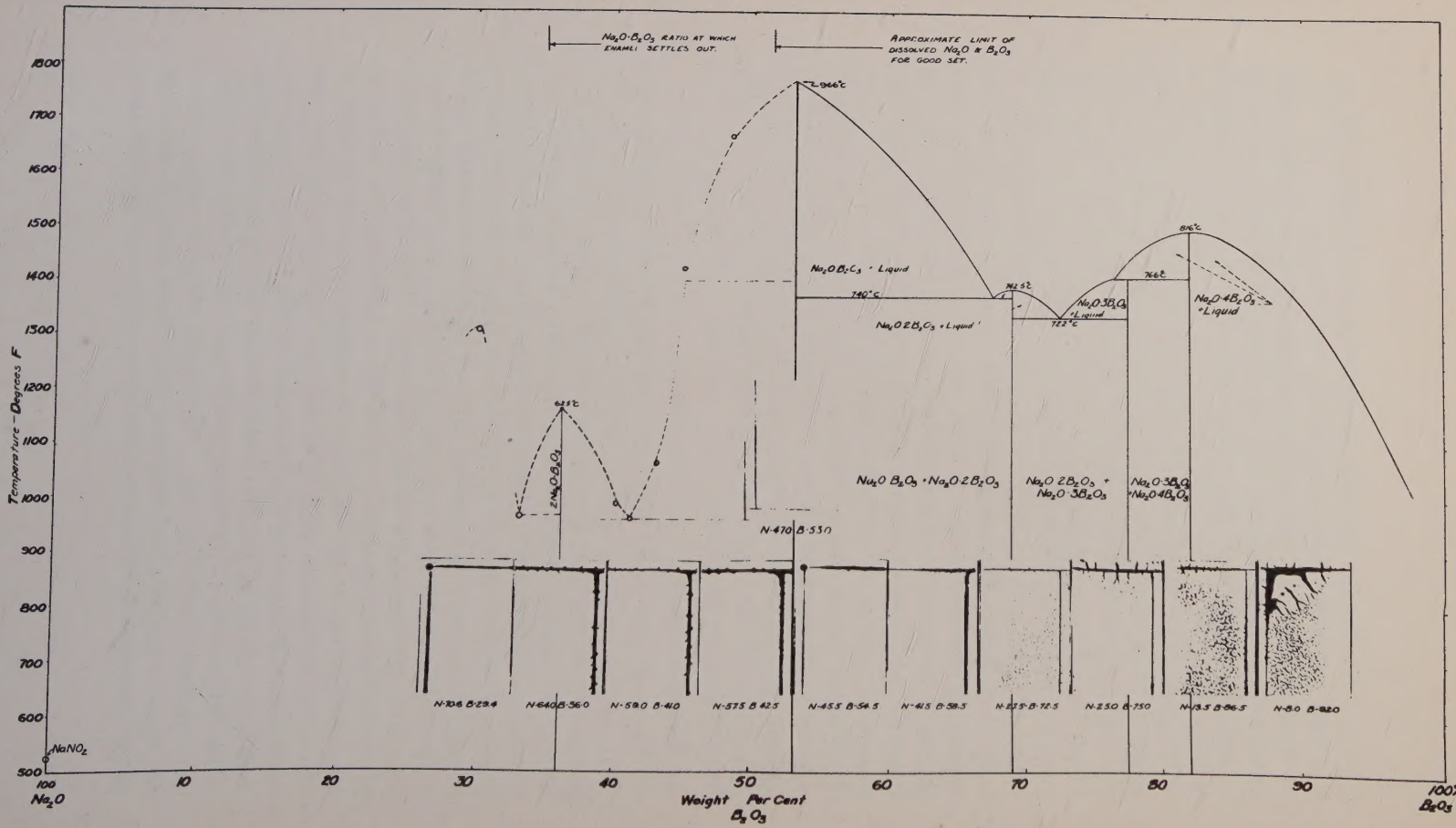

Figure 1. Relation of the Na_2O : B_2O_3 ratio to the tearing resistance of enamel films. Full line diagram after Morey and Merwin[13]; dashed line liquidus as of this study.

the enamel, at the ground coat-cover coat interface and along cracks through the thickness of the film.

Boric acid crystals contain water which is evolved during heating. This dehydration occurs stepwise over a considerable range of temperature, and causes the material to seethe violently and expand to many times the original volume. In the expanded condition these salts possess strong, tough, films. When the enamel is fired, the boric oxide compounds expand and exert lifting and rending forces on the friable, relatively inert, films of enamel. Strains are set up along the cracks and rupture the enamel.

Simultaneously with the expansion of the hydrated boric oxide and the escape of water vapor from beneath the surface, the salt concentrated at the top of the film passes through a similar cycle. Since the salt is near the surface, its moisture escapes more easily and the forces are dissipated without injury to the enamel surface.

Boric acid melts at 561.2° F., and its volume decreases, which may further decrease the mechanical strength of the film.

Because of its high surface tension and relatively high viscosity, melted boric acid causes tearing by drawing the enamel together to form balls. The enamel film already cracked and weakened by the internal forces of expanding boric acid, offers little resistance to the tearing forces of the molten material. Since a thermal gradient exists between the top and under surfaces of the film, there is a time interval between the melting of the boric acid at the top and that below the surface. During this period the two deposits of salt aid each other in the destruction of the enamel. The forces of the sub-surface material lift the film and thereby assist the melt at the surface to roll the film into curls and balls. The melted boric acid at the surface further seals the pores and increases the lifting effect of the escaping gases by reducing their avenues of escape.

Increased time and temperature of firing decrease the effect of boric acid by reducing its surface tension and viscosity, and in addition the strength of the enamel film is increased by fusion of the frit. If enamel films are once cracked or broken, it is difficult for them to heal during firing because of the high surface tension and viscosity of the glass.

In addition to the effects of the surface tensions of the molten salts on tearing, the influence of the viscosities of these melts is of equal importance. Changes in composition and temperature have far greater effects on the viscosities than the surface tensions of such liquids.[15] Since both the quantities and compositions of these

salts vary between wide limits in enamels, and since the temperature changes from room temperature to 1500° F. and higher in the brief time of firing enamels, the viscosities of these molten salts constitute one of the most important factors which control the film strength of enamels.

C. Correction of Tearing

The film strength of enamels is increased and tearing eliminated by maintaining a sodium oxide-boric oxide ratio of 0.89, which corresponds to that of sodium metaborate. Sodium metaborate can be formed by dry fusion of its constituents or by crystallization from solution. Hibbend[16] demonstrated by Raman spectra that the addition of a base to boric acid solutions always formed sodium metaborate until one mole of base was added for each mole of acid. Further additions of base caused no change in the ionization of the system. By the additions of sodium hydroxide, or equivalent sodium to solutions of boric acid, sodium metaborate plus boric acid are produced until equivalents of each material are present. Thereafter the systems contain sodium metaborate and excess basic salt.

Sodium metaborate is many times more soluble than boric acid. During drying of the enamel film, it remains in solution longer and does not congest the capillaries as does boric acid. Consequently the water diffuses to the surface where the salts are ultimately precipitated. Drying takes place more uniformly, cracks rarely form in the film, and the salts are concentrated at the surface. Sodium metaborate is the highest melting compound in the system $Na_2O : B_2O_3$. Its dehydration expansion is much less than that of boric acid, and since the salt concentration is at the surface, volume changes are harmless. Disruption caused by boric acid is most severe between 1000° and 1200° F. because the boric acid is most active and the enamel most fragile during this period. Sodium metaborate causes no tearing since it is itself inert at temperatures below 1300° F. As the film fuses, it gains strength, and the metaborate is taken into solution without evolving any gases to injure the enamel.

In the event that all the boric acid and sodium nitrite or other corrective salts failed to react in the slip, sodium metaborate can be formed during firing. Sodium nitrite melts at a low temperature, forms a very mobile melt of low surface tension, and diffuses through the film. This melt rapidly dissolves and combines with the boric acid, reduces the expansion of the latter, and prevents rupture of the film by removing the boric acid as sodium metaborate.

By forming sodium metaborate with corrective salt additions, boric acid is removed from the system and tearing eliminated.

Contrary to generally accepted ideas that enamel film strength and tearing resistance can be improved by use of low melting electrolytes, it has been shown that this is not always true. Several low melting salts of lithium, potassium, and lead for example, cause severe defects. Brushed edges were masked and run over, the films were easily dislodged, and poor surfaces were developed.

The success of sodium nitrite and the failure of many other salts in eliminating tearing is a function of the anion of the salts. Sodium nitrite forms sodium metaborate in boric acid solutions, and during heating the nitrite portion volatilizes completely without harming the film. Sodium nitrate on the other hand causes severe blistering due to the evolution of gas after the fusion of the enamel. Fluoride salts in general are too refractory and produce scummed and pitted surfaces. For these reasons it is obvious that the choice of salts depends not only on the ability of the salt to form the metaborate, but also on the absence of undesirable characteristics associated with the salt anion.

CONCLUSIONS

1. Solution of the frit is more of a leaching process than a true solution. Of the materials extracted from the frit during milling and which, as salts, concentrate at the film surface during drying, sodium fluoride is the most abundant. Other salts include borax, sodium metaborate, sodium metasilicate, sodium carbonate, sodium sulphate and silica-alumina gel.

2. Because of the high buffering properties of solutions of these salts, the pH values of the mill liquors serve as no criteria for slip control and film strength.

3. The degree of consolidation, or the strength of the dry film is probably influenced by the base exchange capacity of the clay and the kind of cation which is adsorbed. Sodium phosphate facilitates grinding by increasing the total base exchange capacity of the clay through anion exchange of the phosphate.

4. There does not seem to be any definite correlation between the particle size, shape, and size distribution, and enamel film strength, except that coarser particles are more resistant to tearing than finer ones.

5. While many other salts in enamel slips are associated with film strength, the predominating materials responsible for poor film

strength are boric acid and compounds especially high in borate content such as borax.

6. Contrary to generally accepted ideas that sodium nitrite eliminates tearing because of its low melting point, and subsequent bonding of the dry enamel prior to the fusion of the frit, this study has demonstrated that sodium nitrite and other salts prevent tearing by converting the boric acid in the system to the more soluble, higher melting sodium metaborate.

7. From the standpoint of slip control and ease of elimination of the volatile constituent, sodium nitrite is the best salt for introducing sodium ions into the slip. However, many other salts might be employed if suitable precautions are observed in their use.

8. The behaviors of systems of soluble salts such as exist in enamels below the fusion of the frit, definitely influence the brushing qualities, the film strengths and finally the finished surfaces of enamels. The study of these salts as a system, independent of the frit, is a new point of view that was developed by this investigation. This concept offers an opportunity for further research in the study of the film strength of enamels.

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VITA

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The writer is a member of Phi Kappa Phi, Tau Beta Pi, Keramos, Sigma Xi, the American Ceramic Society, and the Sigma Nu fraternity.

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